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SEAWATER DEOXYGENATION: PROBLEM OR SOLUTION?

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Background and Motivation: Laboratory experiments were designed to test the hypothesis that oxygen is required for aggressive corrosion of carbon steel exposed to natural seawater. Uncoated carbon steel was maintained for 1 year under the following stagnant conditions: (1) natural seawater open to air, and (2) anaerobic natural seawater stripped of oxygen. Hamilton¹ recently proposed a model for corrosion of carbon steel due to anaerobic sulfate-reducing bacteria (SRB) in which sulfate, an intermediate electron acceptor, is reduced to sulfide. In his model, sulfide reacts with iron to form a corrosion product that ultimately transfers electrons to oxygen. Consistent with that model, most reported cases of aggressive SRB-induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium. However, Hamilton's theory does not address corrosion rates in anaerobic waters with multiple electron acceptors.

Experimental Chambers: Chambers were built to expose carbon steel to natural seawater with and without oxygen (Fig. 10). Epoxy-mounted carbon steel coupons were oriented in rows both vertically and horizontally to simulate tank sidewalls and bottoms, respectively. Chambers were filled with natural seawater from the Naval Research Laboratory's Corrosion Facility at Key West, Florida. Seawater was deoxygenated using a premixed inert gas containing CO₂. The chamber filled with natural, oxygenated seawater was open to air via a 1-in. tube. The chamber filled with anaerobic water was maintained in an anaerobic hood with an atmosphere of 5% CO₂, 10% H₂, and the balance N₂.

Electrochemical Methods and Results: Open-circuit potential (E_{corr}) was monitored continuously, and linear polarization resistance (LPR) measurements used to determine polarization resistance (R_p) were performed on each sample every 1-3 months. The inverse ($1/R_p$) is the proportional instantaneous corrosion rate, given in ohms⁻¹. Figure 11 shows the average E_{corr} values by row. E_{corr} values for all samples started at approximately $-0.75 \text{ V}_{\text{Ag/AgCl}}$. No appreciable difference in E_{corr} was observed as a function of placement

in the aerobic chamber. In contrast, stratification of E_{corr} values was observed between rows in the anaerobic chamber. $1/R_p$ values, calculated for each electrode, were averaged by row and exposure type (Fig. 12(a), (b)). Between 23- and 35-days, corrosion rates for all samples were relatively low with the lowest in the anaerobic chamber (Fig. 12(c)). At the same time, $1/R_p$ values indicated stratification within the aerobic chamber. Row 1 electrodes, closest to the air/water interface, had the highest average corrosion rate, while row 4 electrodes had the lowest. After more than 100 days exposure, the $1/R_p$ measurements indicated that the highest instantaneous corrosion rate was measured in the horizontal (bottom, row 4) coupons exposed to anaerobic seawater. In general, instantaneous corrosion rates for the anaerobic condition were two orders of magnitude higher than the aerobic condition.

Corrosion Morphology: Corrosion products formed under aerobic and anaerobic seawater conditions were predictably different in appearance and composition. Under aerobic conditions, iron oxides persisted on the surfaces of all coupons/orientations throughout the experiment and corrosion was uniform. Coupons exposed in anaerobic seawater were covered with black iron sulfide corrosion products and corrosion was localized (i.e., pitting). Iron sulfides are inherently unstable, and their disruption can give rise to corrosion cells between iron sulfide in direct electrical contact with the underlying steel (cathode) and the exposed-steel surface (anode).

Consequences of Deoxygenation: Experiments described here demonstrate that corrosion of carbon steel is more aggressive under totally anaerobic conditions compared to exposures in oxygenated seawater. Corrosion was more severe on the horizontally oriented samples than on the vertically oriented coupons in both exposure conditions. Corrosion of carbon steel exposed under totally anaerobic conditions was typical microbiologically influenced corrosion by sulfate-reducing bacteria (SRB). Microbial populations increased over 5 orders of magnitude in the anaerobic chamber. Hamilton¹ concluded that the activities of microorganisms produced kinetically favored pathways of electron flow from the metal anode to the universal electron acceptor, oxygen. He observed that microbial ecosystems are characterized by aerobic and anaerobic zones that operate as a continuum via redox couples. Interactions between oxygen and sulfate depend on redox cycling via intermediate electron carriers. Hamilton further stressed that biofilm growth is a dynamic process and microorganisms within the biofilm are in

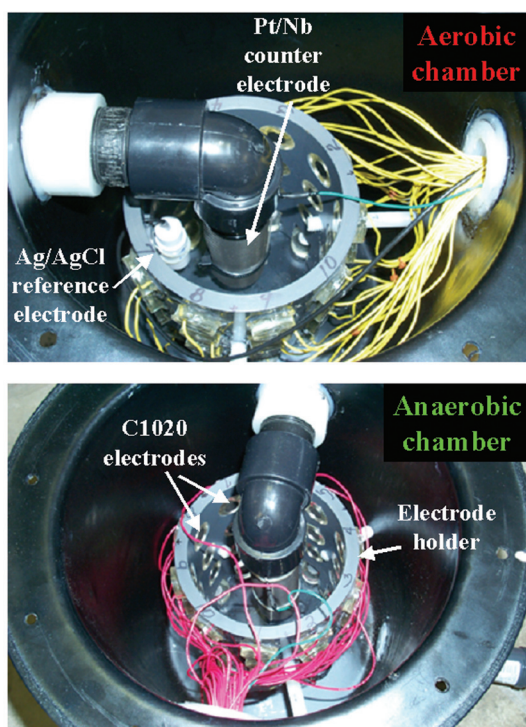
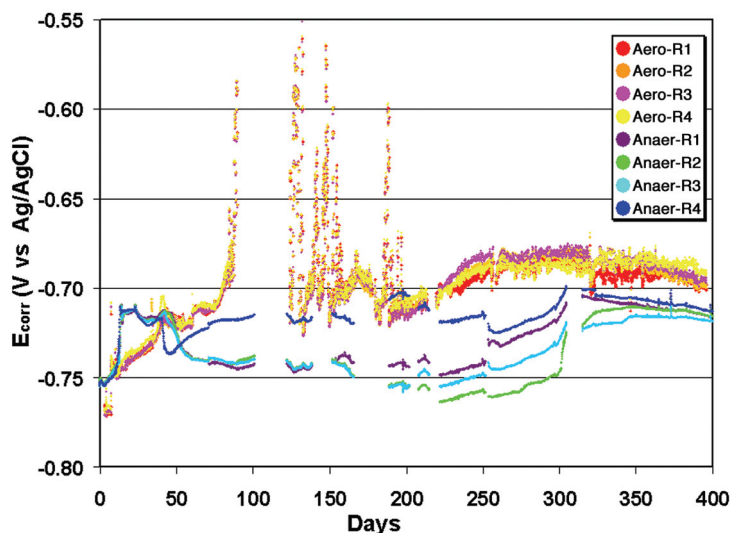


FIGURE 10

Heavy gauge plastic experimental chambers each containing Ag/AgCl reference electrode, Pt/Nb mesh counter electrode, cylindrical electrode holder, and 36 individually addressable C1020 electrodes (27 vertically orientated, 9 horizontally orientated).

FIGURE 11

Average E_{corr} (vs Ag/AgCl) over time values for C1020 samples in stagnant aerobic (aero) and anaerobic (anaer) conditions displayed by row (R). R1, R2, R3 – vertically orientated samples, with R1 being at the top of the tank, R3 toward the bottom, and R2 between the two. R4 – horizontally orientated sample at the bottom of the tank.



a constant state of flux. Individual bacterial species and bacterial consortia are characterized by their primary energy source and electron donor and terminal electron acceptor. Oxygen is the terminal electron acceptor for aerobic species, but for anaerobic species (e.g., SRB) there are alternate electron acceptors, including nitrate, sulfate, ferric iron, and CO_2 . It is possible that in the complex chemistry of seawater and biofilms there are electron acceptors other than oxygen to drive electron transfer and corrosion reactions.

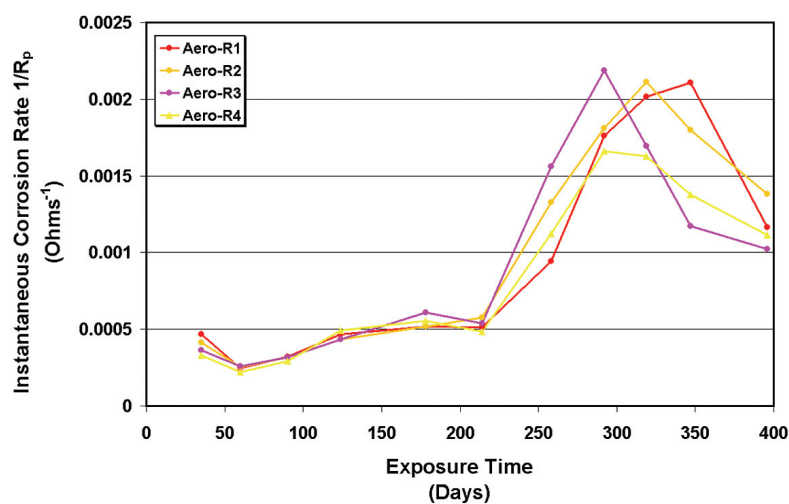
Summation: Corrosion of carbon steel was more aggressive in totally anaerobic conditions than in aerobic conditions. Anaerobic conditions did not

inhibit corrosion, and oxygen was not required for aggressive localized corrosion. This work indicates the danger of predicting long-term corrosion involving deoxygenation in short time periods (less than 1 month) where results indicate deoxygenation is favorable, as opposed to extended periods where SRB can instigate localized corrosion.

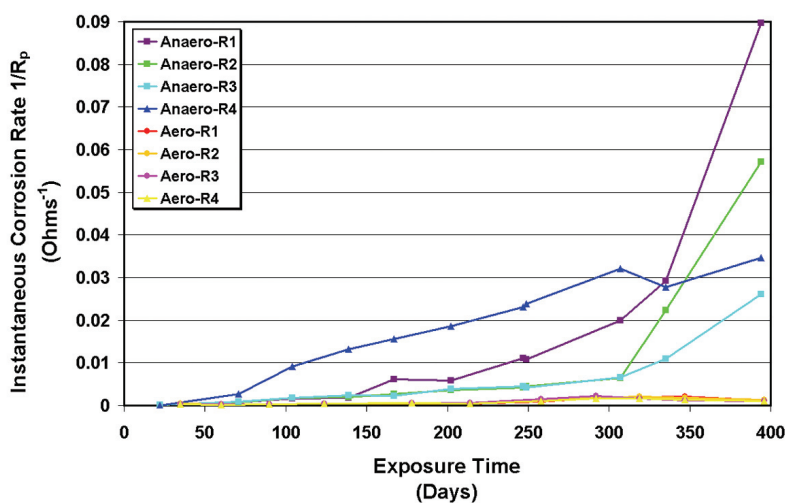
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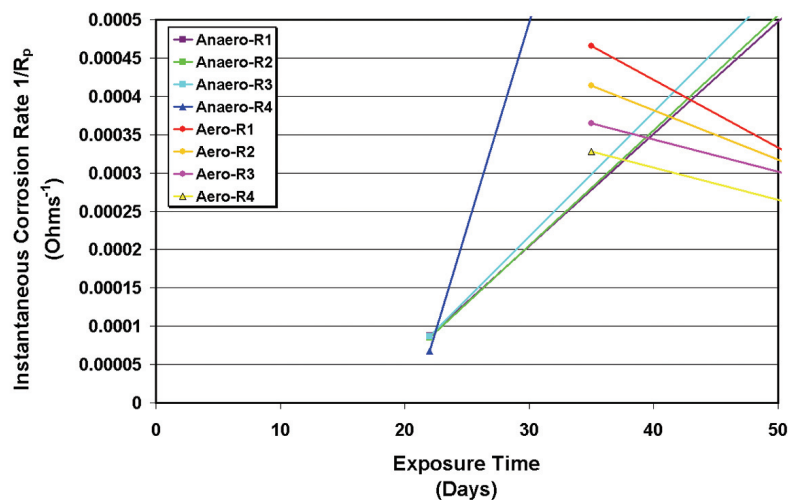
- ¹ W.A. Hamilton, "Microbiologically Influenced Corrosion as a Model System for the Study of Metal Microbe Interactions: a Unifying Electron Transfer Hypothesis," *Biofouling* **19**, 65-76 (2003).



(a)



(b)



(c)

FIGURE 12

$1/R_p$ (instantaneous corrosion rate) over time (days) for C1020 samples in stagnant (a, b) aerobic and (b) anaerobic conditions. Aerobic conditions are included with anaerobic data (b) to indicate the much higher rates in anaerobic conditions. Early corrosion rates are shown in (c) for both aerobic and anaerobic conditions. R1, R2, R3 – vertically orientated samples, with R1 being at the top of the tank; R3, toward the bottom, and R2 between the two. R4 – horizontally orientated sample at the bottom of the tank. Average values displayed.